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Synthesis and catalytic properties of nickel salts of Keggin-type heteropolyacids embedded metal-organic framework hybrid nanocatalyst

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Abstract: Nickel salts of Keggin-type heteropolyacid on Zr(IV)-based metal-organic frameworks (UiO-66) has been synthesized via ion-exchange followed by a facile one-pot hydrothermal method. The synthesized catalysts underwent FT-IR, N_2 adsorption-desorption, powder XRD, SEM and TEM analysis. The NiHSiW/UiO-66 catalyst was used as a new and effective solid acid in the catalytic transfer free fatty acid to biodiesel with an optimum conversion of 86.7%. The excellent activity of the NiHSiW/UiO-66 nanocatalyst was closely related to its high specific surface area, nano-sized catalyst, and the synergistic effects of NiHSiW salts and UiO-66 matrix. Importantly, a relatively stable catalytic performance was achieved for 8 repeated cycles. Finally, kinetics of the esterification reaction have been assumed to be of pseudo first order.

Keywords: heteropolyacid salts; UiO-66; nanocatalyst; esterification; biodiesel

1 Introduction

In the last few years, there has been increasing interest in the production of renewable fuels or chemicals, owing

to decreased fossil fuels resources and increased severe environmental pollutions [1-3]. Biodiesel (fatty acid methyl esters, FAMES) is gaining popularity as an alternative fuel due to its availability, more biodegradable, lower emissions of CO, non-toxic and renewable fuels [4,5]. Currently, biodiesel is produced by esterification/ transesterification of edible vegetable oils, non-edible oils, waste oils or algal oils using homogeneous acid and base catalysts [6,7]. However, this homogeneous process suffers from several disadvantages including a non-reusable catalyst, the high production cost for purification, and produce a lot of wastewater [8]. To avoid the above problems and to save the production cost, there is a growing trend in the field of solid catalysts for biodiesel production.

Solid catalyst can be easily separated by simple physical processes, recyclable, and simplicity of biodiesel purification [9]. A variety of solid base catalysts were used, e.g. CaO-based PKSB [10], magnetic nanoparticle $MgFe_2O_4@CaO$ [11], CaO/SiO_2 [12], etc. However, they were more or less submitted to drawbacks of sensitivity to free fatty acids and water resulting in catalyst poisoning, and the occurrence of undesired soaps [13]. For these issues, the development of solid acid catalyst is an interesting approach to produce catalysts for the production of biodiesel.

Various types of solid acid catalysts have been utilized in biodiesel production. These solid acids include ferric-modified phosphomolybdic acid composite [14], lipase immobilized on graphene oxide Fe_3O_4 nanocomposite [15], polymeric acidic IL-functionalized Fe_3O_4/SiO_2 [16], sulfonated graphene [17], $Fe_3O_4@HKUST-1$ -ABILs [18], sulfonated ordered mesoporous carbon [19], and few supported catalysts such as $H_3PW_{12}O_{40}$ -Ni/hierarchical mesoporous zeolite Y [20]. Based on previous researches, metal-organic frameworks (MOFs) can serve as a promising catalyst supports, due to the distinctive porous structure, high surface area, and possess relatively stable [21]. More interestingly, MOFs are highly designable, tunable host-guest interactions. To date, the encapsulation of heteropolyacids into MOFs has attracted many interests as a composite catalyst, such as $PMoV@MOF$ [22], bi-functional polyoxometalate-MIL-101 [23],

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AILs/HPW/UiO-66-2COOH [24]. In this regard, the zirconium-based UiO-66 has been extensively investigated as a desirable host matrix closely related to its chemical stability as well as significantly robust thermal [25]. According to our previously reported study, we prepared the silicotungstic acid encapsulated on UiO-66 for biodiesel production from lauric acid and methanol, and showed the high conversion of 92.8% [26]. To the best of our knowledge, the encapsulation of nickel salts of Keggin-type heteropolyacids into UiO-66 for produce biodiesel have not been conducted yet. Herein, a catalysts made of nickel salts of Keggin-type silicotungstic acid encapsulated in UiO-66 was proposed for biodiesel synthesis from oleic acid. Characterisation and application investigations of this novel composite catalyst are also studied. Furthermore, reusability and kinetic study of the composite catalyst was investigated in detail.

2 Materials and methods

2.1 Materials

All chemicals were obtained from Sinopharm Chemical Reagent Co., Ltd. and used as received without any further purification. Zirconium(IV) chloride (AR), terephthalic acid (AR), silicotungstic acid ($\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, AR), nickel (II) nitrate hexahydrate (AR), oleic acid (AR), methanol (AR, >99%).

2.2 Preparation of NiHSiW/UiO-66

Nickel salts of Keggin-type heteropolyacids supported on metal organic framework were synthesized via a facile one-pot hydrothermal method according to the following procedure [27]. H_4SiW (1440 mg) were dissolved in deionized water, then nickel (II) nitrate (70 mg) aqueous solution was added dropwise at 70–80°C under constant stirring for 3 h. Subsequently, the formed solid (denote as NiHSiW), zirconium (IV) chloride (2.2 mmol), and terephthalic acid (2 mmol) were added together in 18 mL of N, N-Dimethylformamide (DMF) solution and stirred for another 3 h. The obtained mixture was sealed and heated at 120 °C for 6 h in a 50 mL Teflon-lined autoclave. After 6 h, the resulting solid was filtered off and purified by using around 50 mL of DMF and 50 mL of ethanol. Then dried under vacuum for overnight at 80°C. The obtained sample was designated as NiHSiW/UiO-66. In addition, the UiO-66 was also prepared according to the hydrothermal

method without NiHSiW. Before the catalytic esterification reaction, the composite catalyst was dried in vacuum at 120°C for 2 h.

2.3 Characterization of NiHSiW/UiO-66

X-ray diffraction (XRD) analysis was performed on D8 ADVANCE (Germany) using $\text{CuK}\alpha$ (1.5406 Å) radiation. Fourier transform infrared (FT-IR) spectra were collected with Spectrum 100 (PerkinElmer) using an attenuated total reflectance (ATR) accessory, and used to analyze different functional groups with the range from 4000 to 400 cm^{-1} . N_2 physisorption of each sample was determined by a Quantachrome Quadrasorb EVO apparatus (Quantachrome Instruments, Boynton Beach, USA). The morphologies of the samples were observed by scanning electron microscope (SEM) (Hitachi, S4800) and Transmission electron microscopy (TEM) (FEI Tecnai G2 20), respectively.

2.4 Performance testing of NiHSiW/UiO-66

All these esterification reactions in this work were performed in a 50 mL stainless-steel high-pressure autoclave reactor, oil bath and magnetic stirring system. The reaction mixtures, 3.0 g of oleic acid, methanol and the NiHSiW/UiO-66 catalyst are fed into the autoclave reactor, and then the reaction mixture was agitated at desired temperature. After the completion of reaction, the liquid products were collected after the centrifugation of the solid-phase catalysts. Thereafter, methanol and water were removed using rotary evaporation in order to purify the product. The conversion of oleic acid were calculated from acid value (AV) using equation:

$$\text{Oleic acid conversion (\%)} = \frac{AV_1 - AV_2}{AV_1} \times 100\% \quad (1)$$

where AV_1 and AV_2 are the acid value of oleic acid and reaction products, respectively. The acid value analysis by titration method according to the ISO 660-2009 standard.

3 Results and discussions

3.1 Properties of NiHSiW/UiO-66

The FT-IR spectra of the H_4SiW , NiHSiW, UiO-66 and NiHSiW/UiO-66 samples are presented in Figure 1a. The

FT-IR spectra of H_4SiW and $NiHSiW$ are consistent with previously reported results [28,29]. In the case of $NiHSiW$ and $NiHSiW/UiO-66$ samples, the stretching vibrations absorption peaks of $W=O$, $Si-O$, $W-O_c-W$ and $W-O_e-W$ are observed at 980, 927, 884 and 804 cm^{-1} , respectively, which is associated with the Keggin structure. By contrast, the spectrum of $NiHSiW/UiO-66$ sample is similar to that of the $UiO-66$, implying the structure of $UiO-66$ was not changed after the encapsulation of $NiHSiW$ into the cages of $UiO-66$. These results suggested that the $NiHSiW$ salts were present on $UiO-66$ samples. The XRD pattern of the $UiO-66$, $NiHSiW$ and $NiHSiW/UiO-66$ samples were shown in Figure 1b. As contrast, some diffraction peaks for the $NiHSiW$ were overlapped with those of $UiO-66$ support, and the phase structure of the $UiO-66$ (2θ , 7.2° , 25.7° , 43.5° , 50.2°) and $NiHSiW$ (2θ , 7.2° , 25.7° , 30°) mainly exists in the $NiHSiW/UiO-66$ sample, which can be concluded to the $NiHSiW$ embedded in cages of $UiO-66$. Noteworthy, some XRD diffraction peaks for

$NiHSiW$ were no found for the $NiHSiW/UiO-66$ catalyst, it may be associated with interaction between $NiHSiW$ and $UiO-66$ support.

The N_2 adsorption and desorption isotherms and BJH pore size distribution of $UiO-66$ and $NiHSiW/UiO-66$ are shown in Figures 2a and 2b. As shown Figure 2a, the result demonstrates that the adsorption isotherms of the $UiO-66$ was change after the encapsulation of $NiHSiW$. Meanwhile, the $UiO-66$ sample show a type I isotherm, meaning that the existence of a microporous structure. However, the $NiHSiW/UiO-66$ composite exhibit type IV isotherm, and the Hysteresis loop at the P/P_0 of 0.45-1.0 indicated typical mesoporous structures. In addition, the as-prepared $NiHSiW/UiO-66$ have a high specific surface area ($692.3\text{ m}^2/\text{g}$) and average pore size (4.40 nm) than that of the $UiO-66$ sample (specific surface area of $667.2\text{ m}^2/\text{g}$ and average pore size of 2.58 nm). This is probably due to the successful introduction of the $NiHSiW$ salts, and a strong interaction effects of the salts

Figure 1: (a) FT-IR spectra in the region from 2000 to 450 cm^{-1} with H_4SiW , $NiHSiW$, $UiO-66$ and $NiHSiW/UiO-66$ samples; (b) XRD spectra of $UiO-66$, $NiHSiW$ and $NiHSiW/UiO-66$ samples.

Figure 2: (a) N_2 adsorption-desorption isotherms and (b) pore size distribution of $UiO-66$ and $NiHSiW/UiO-66$ catalysts.

and host matrix, which are in good accordance with FT-IR and XRD results.

The SEM micrographs of the H_4SiW , $NiHSiW$, $UiO-66$ and $NiHSiW/UiO-66$ samples are presented in Figures 3a-d. As was shown, the H_4SiW sample (Figure 3a) have a bulk of massive structure with a not obvious pore structure. After doped the nickel ions, the aggregates of the small irregular lumpy structure can be found (Figure 3b), this is probably because the exchange of protons with nickel ions. In the case of the $UiO-66$ sample, the morphology of catalyst (Figure 3c) exhibited near-spherical shapes from our previously reported [26]. When $NiHSiW$ was incorporated with $UiO-66$ material, the morphology of the $NiHSiW/UiO-66$ is obtained somewhat similar to that of $UiO-66$ material (Figure 3d), it displayed a numerous nanoparticles

structure and with no significant aggregation of $UiO-66$ crystallites, which is might due to strong $NiHSiW$ -matrix interaction, resulting in the cooperative effects for enhancing the catalytic activity. These data mentioned above indicated that the $NiHSiW$ salts was embedded in the framework of $UiO-66$.

The morphology of the $UiO-66$ and $NiHSiW/UiO-66$ samples were further analyzed by TEM (Figures 4a-c). The $UiO-66$ has a relatively regular shape, showing a near-cubic structure. As contrast, Figures 4b and 4c show $NiHSiW/UiO-66$ exhibited the near-cubic crystal structure and an average side length of around 100 nm. Of note, the obtained structure was found similar to that of the original structure of $UiO-66$, which further confirmed the strong stability of $UiO-66$, and are accordant with SEM results.

Figure 3: SEM images of H_4SiW (a), $NiHSiW$ (b), $UiO-66$ (c) and $NiHSiW/UiO-66$ (d) catalysts.

Figure 4: TEM images of $UiO-66$ (a) and $NiHSiW/UiO-66$ (b,c) catalysts.

3.2 Reactions

3.2.1 Influence of time and temperature

To study the reaction time influence, the oleic acid esterification reaction was investigated by varying the reaction time from 0.5 to 4.0 h. As displayed in Figure 5a, the oleic acid conversion is only 24.5% at 0.5 h, and then increased to 86.7% as the reaction time is increased to 3.0 h. However, the conversion of methyl oleate rising slowly with prolonging the reaction time. Hence, the optimum reaction time is chosen 3.0 h for further experiments. Additionally, the temperature was also a significant factor affecting esterification reaction. In this study, it was different temperature of 100–170°C to study its influence on oleic acid conversion. As observed

in Figure 5b, a considerable increase in the oleic acid conversion was achieved the increase in the reaction temperature from 100°C to 160°C. Further increase of temperature to 170°C, there is no significant change in oleic acid conversion. Therefore, the optimum reaction temperature was selected to be 160°C.

3.2.2 Influence of oleic acid to methanol molar ratio and catalyst amount

The stoichiometric molar ratio of oleic acid to methanol for esterification is 1:1, and the esterification process is reversible reaction. Thus, in order to shift the equilibrium conversion of the reaction, excess methanol is normally required. As illustrated in Figure 6a, this clearly shows that

Figure 5: Effect of (a) reaction time (molar ratio of oleic acid to methanol: 1:18, catalyst amount: 180 mg, and reaction temperature: 160°C) and (b) reaction temperature on esterification of oleic acid (molar ratio of oleic acid to methanol: 1:18, catalyst amount: 180 mg, and reaction time: 3.0 h).

Figure 6: Effect of (a) oleic acid to methanol molar ratio (catalyst amount: 180 mg, reaction temperature: 160°C, and reaction time: 3.0 h) and (b) catalyst amount on esterification of oleic acid (molar ratio of oleic acid to methanol: 1:18, reaction temperature: 160°C, and reaction time: 3.0 h).

with an increase in the oleic acid to methanol molar ratio from 1:6 to 1:18, the oleic acid conversion increases from 72.7% to 86.7%. However, beyond an oleic acid to methanol molar ratio of 1:21, the excess amount of methanol had no significant effect on the oleic acid conversion. Meanwhile, the recovery of the excess methanol is also obligatory and the need of a high of cost. Therefore, the optimum molar ratio of oleic acid to methanol was 1:18. In addition, the influence of catalyst amount on esterification was also studied. And as may be observed from Figure 6b, the conversion of oleic acid increased with rising catalyst amount. The better oleic acid conversion was achieved when catalyst amount of 180 mg, and then the conversion of oleic acid began to slight decrease, this may be because the excess of catalysts can resist the mass transfer in the heterogeneous reaction system. Similar behavior was observed by Jin et al. [30]. Therefore, the appropriate catalyst amount is 180 mg.

3.3 Reusability of the NiHSiW/UiO-66 nanocatalyst

The catalytic stability of the NiHSiW/UiO-66 was evaluated in esterification reaction. After the completion of reaction, the NiHSiW/UiO-66 catalyst was separated by centrifugation, washed by methanol, and immediately used for next reaction. As displayed in Figure 7, it can be concluded that the catalytic activity of NiHSiW/UiO-66 catalyst is relatively retained in eight successive runs with around 50% conversion. FT-IR analysis of the structure of fresh catalyst and after eight-times used are similar (Figure S1 in Supplementary material), meaning

Figure 7: Reusability performance of the NiHSiW/UiO-66 nanocatalyst on the conversion of the esterification reaction (molar ratio of oleic acid to methanol: 1:18, catalyst amount: 180 mg, reaction temperature: 160°C, and reaction time: 3.0 h).

that the Keggin structure was maintained. In addition, the reduction of catalytic performance is might due to the gradual leaching of catalyst during repeated reactions, and the loss of catalyst of the collecting operation in each consecutive cycles, similar with those reported in the literature [31]. The obtained results indicate that the prepared NiHSiW/UiO-66 catalyst is relatively stable for biodiesel production.

3.4 Kinetic studies

A kinetic study of the esterification of oleic acid catalyzed by NiHSiW/UiO-66 was determined by varying different temperature (100°C, 130°C, 160°C), and as illustrated in Figure S2. Meanwhile, the time (h) vs $-\ln(1-X)$ (where X is the oleic acid conversion) plot on diverse reaction temperatures to get the reaction rate constants (k), and as shown in Figure S3. From Figure S3, the figure gives the straight line, this confirms the esterification process of oleic acid using NiHSiW/UiO-66 follows the first order kinetic model. It was clearly seen that the reaction rate rises with rise in temperature, indicating the higher temperature accelerates the esterification rate. The activation energy E_a was calculated from the plot of $\ln k$ vs $1/T$ (K) as displayed in Figure 8. The highest activation energy was found for NiHSiW/UiO-66 (69.2 kJ/mol), implying that the reaction is chemically controlled due to the limitation mass transfer or diffusion process. Of note, the E_a value obtained in the present study is lower with than previous studied (The E_a for biodiesel production is 161 kJ/mol) [32]. Based on this, this further confirms the excellent catalytic activity of the NiHSiW/UiO-66 hybrid nanocatalyst for the esterification process in this study.

Figure 8: Arrhenius plot of the esterification of oleic acid with methanol over NiHSiW/UiO-66 to obtain the activation energy (E_a).

4 Conclusions

A green, ecofriendly and reusable solid acid catalyst was developed by a simple one-pot hydrothermal method. The synthesized NiHSiW/UiO-66 nanocatalyst with a higher surface area (692.3 m²/g) exhibited excellent catalytic performance for biodiesel production from oleic acid. A high oleic acid conversion of 86.7% was obtained at the optimized conditions. In the 8th cycle, a conversion of 50% was achieved. Besides, the esterification process followed pseudo first order kinetics, and the activation energy (69.2 kJ/mol) was found to be non-spontaneous. Therefore, these results demonstrate that developed NiHSiW/UiO-66 catalyst can be considered as an attractive alternative respect to the liquid acid catalysts for the production of biodiesel. This technology could be used at industrial scale, however, future works must be performed to explore this question.

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